Material Contained herein is Proprietary to J.C. Systems and J.J. Cronin

TITLE: Hypergolic Hydrogen Generation System for Fuel Cell Power Plants

Inventor(s): J. Cronin of Niwot, Colorado

Abstract: This patent application presents a process whereby applying a controlled hypergolic approach using Hydrogen Peroxide in the form of High Test Peroxide (HTP) in combination with certain hydrocarbons such as Ethanol, Methanol, Methane, etc. one can generate a gas mixture containing basically hydrogen and carbon dioxide. The process is executed in a constraining system on a microscale level in a manner such that the resulting hydrogen supply is self-pressurizing and operates without the need of an external air supply.

When implemented in an automotive environment it can enable the incorporation of an "on demand" hydrogen fuel operation for a variable output Fuel Cell Power Plant. This avoids the complications involved in the miss-match existing in the delivery turndown capabilities that exist between potential current on board hydrogen generation and air supplies into the Fuel Cell Stack. It avoids having to have a large mass of hydrogen gas stored at high pressures (5-10,000 psi) in order to achieve a range desired for reasonable consumer use. This storage means has

been the result of the inability of current onboard reforming systems to activate in a reasonable time and be ready to deliver the needed hydrogen.

In addition, the process when implemented in a stand alone stationary or transportable configuration can be used as a refueling system for those automotive or other commercial applications when it is desired to do on-site H_2 commercial generation, or to just have a hydrogen source available for other purposes.

Field of the invention:

This invention relates to Fuel Cell Power Systems (FCPS), especially with regard to on board reforming, and the storage and metering of Hydrogen. It does this in a manner that resolves the dynamic turndown ratio differences between the air subsystem delivery needs for the Fuel Cell Stack and for Fuel Reformer air needs with its differing turndown capability that presents control system challenges. It does this by recognizing that what the fuel reforming process needs is Oxygen only since the other make-up gases of air are what causes much additional cleanup efforts on the part of a total FCPS.

Background of the invention:

Fuel Cell Powering Systems (FCPS) have the potential to become an economically viable means of converting chemical energy to electrical energy. For example, in a polymer-electrolyte membrane (PEM) fuel Cell, also known as a proton exchange membrane fuel cell, Hydrogen and Oxygen are the elements to be combined for production of electrical energy. Air is the customary source of oxygen while the oxidant can be any hydrogen fuel stock including hydrogen, methane, natural gas and ethanol. Other than pure hydrogen the fuel source may require a local refining process to produce the hydrogen in a form acceptable to the PEM membranes in the stack. The device for accomplishing this is called a reformer. The energy conversion in the fuel cell occurs through a process of oxidation, which relies upon the pressurization of both the oxidant and the oxidizing agent.

Electrical powering systems utilizing fuel cells are comprised of several subsystems requiring the compression of air and/or other gases in order to operate. Currently each of these subsystems operates best under distinctly different pressure profiles. As a result, the common approach is to utilize a complete gaseous supply system, including a compressor, a drive motor, a motor controller and perhaps an expander for each subsystem in order to meet the unique pressure of each. Such a solution, is a significant source of cost, size and inefficiency since it creates a large parasitic electrical power draw on the overall FCPS. The reforming subsystem consumes approximately 1/4th of the air requirement of the overall FCPS and is

also the source of the very high pressure required of the air subsystem. This invention purports to obtain system cost reduction and simplification through supplying oxygen via another source thus reducing the requirement of the air compressing system in terms of mass delivery and reduction of the dynamic range of compression needed from the compressor. It will also eliminate the cost of the expander and downsize the drive motor requirements.

To eliminate/avoid the need for providing air to the reformer we use Hydrogen Peroxide (H_2O_2). Here the mass of oxygen in each molecule is 94% (and is in liquid form) versus air. Oxygen makes up about 23% of air mass and is in gaseous form thus requiring a higher volume flow and compression to achieve the required rate of consumption to be useful in the Reformer and Fuel Cell Stack. By using Hydrogen Peroxide mixed with water as the oxidant and such hydrocarbons as Ethanol, Methanol or Methane etc. on a microscale size and in a micro-controlled fashion in the presence of a catalyst, favoring the formation of carbon dioxide, we have a gaseous resulting make-up of CO_2 and H_2. In PEM stacks CO_2 is non-poisonous and contributes to the pressure on the fuel delivery side of the stack, while H_2 is the desired gas for the conversion to electrical power.

Over many decades Hydrogen Peroxide (H_2O_2) has been used as a source of oxygen for combustion of hydrocarbon fuels and generating steam and other gases

used to propel rockets. In addition it has been successfully used as an oxygen source in submarines as early as the 1930's.

Summary of the invention

The present invention takes advantage of the hypergolic reaction nature of Hydrogen Peroxide (in the form of High Test Peroxide (HTP)) when combined with hydrocarbon fuels in an appropriate stoichiometric ratio to produce carbon dioxide and hydrogen. By microinjecting the fuels, in an appropriately timed manner, into a pressure vessel containing a catalyst that encourages the formation of CO_2, we also form another gas product, H2, which is the desired gas for fuel cell use.

If we take the simplest hydrocarbon molecular makeup of combining methane, or methanol, or ethanol with HTP (and eliminating any air) the respective balanced equations are:

$$H_2O_2 + CH_4 \rightarrow CO_2 + 3H_2$$

$$H_2O_2 + 2CH_3OH \rightarrow 2CO_2 + 5H_2$$

$$H_2O_2 + C_2H_5OH + H_2O \rightarrow 2CO_2 + 5H_2$$

It is to be noted that if the water is added to the ethanol/HTP process the yield is the same as the methanol/HTP process. Further more, ethanol is miscible with water, as is HTP, and most likely a preferred configuration for handling in commerce. This process patent will concentrate on describing the use of ethanol as the fuel since it is in the preferred consumer handling form. The other hydrocarbons shown at this time only require adjustments in the respective component operational controls and component configurations to achieve the desired delivery of H2 in a fuel cell power system.

The table below presents, for the balanced chemical equation shown above the table is based upon using ethanol, the rounded molecular weight of the element contained in the reactant (ethanol) of the equation shown at the top of the table.

$$C_2H_5OH + H_2O_2 + H_2O \rightarrow 2CO_2 + 5H_2$$

Element	Ethanol	HTP	Water	Carbon dioxide	Hydrogen
C	24			24	
H	6	2	2		10
O	16	32	16	64	
G/mol	46	34	18	88g=2moles	10g=5moles

Total grams are balanced i.e. 98 = 98

When we look at the HTP mixed with all the water we see the ratio is 34/52 or ≈65%, which is a common form for transporting and handling hydrogen peroxide. At this level it will be hypergolic when mixed with hydrocarbons. Therefor, ethanol will have such a reaction resulting in H2 generation.

Heat is also generated in the process. This heat contributes to the generation of pressure within the confined vessel (P=nRT/V for each gases partial pressure) since the volume of the reaction vessel is fixed. The hypergolic materials injected into the reaction pressure vessel are at the microgram level per pulse and occupy milliliter size volume. The heat generated by the total reactions (deformation as liquids and then reformation as gases) elevates the vessel pressure & temperature.

Since one does not have to use the vessel 1 resulting gases immediately, they sit in this container with the catalyst(s) until they form the desired CO2 while the remaining gas is H2. This avoids the problems of needing an air source to supply the oxygen, and needing a compressor to pressurize the air to the level needed for onboard reforming (≈3.2 bar) as well as a large gas cleanup systems post reformation. Thus downsizing the fuel cell air system requirements by approximately 25% lowering the overall cost of that subsystem. In addition, CO_2 in the gas stream does not harm/poison the fuel cell membranes. The resulting volume of Ethanol and HTP/water combined is approximately equal to today's gasoline volume carried onboard a car with the only difference being that it is divided into two separate tanks.

Brief Drawing Description(s):

Figure 1 -Is a Simplified block diagram of a Fuel Cell Power System that would incorporate a basic Hypergolic Hydrogen Generation System as its source of H2.

Figure 2 – Provides an expanded flow diagram of the Reformer Fuel Supply Subsystem portion of an overall system and references the interfacing parts of the Fuel Cell Power System

Figure 3 – Presents The Reforming Pressure Vessel (#1) Subsystem as well as referencing those parts of the fuel feed system and the output to storage vessel (2)

Figure 4 - Shows the storage pressure vessel (#2) its sensor pack, programmable pressure regulator valve and output to Fuel Cell Stack

Detailed Description:

Figure 1 is a simplified block of the ultimate Fuel Cell Power System. It would have the Hypergolic Hydrogen Generating System divided into three basic subsystems. The Reformer Supply subsystem, a Reforming & Pressure Vessel and the Storage & Delivery subsystem. Each of these subsystems will be further described in conjunction with their individual figures (2, 3, & 4). The reformer supply system provides HTP and Ethanol using a minimum of one injector for each fluid under control of the FCPS Controller to a pressure vessel. Its liquid fuels are pumped using a shaft or 2 if required, from the Air Subsystem driveline. They are injected Said pressure vessel contains a catalyst that encourages the formation of Carbon Dioxide. The fact that the reformer does not have to immediately deliver its products to the Storage & delivery system allows the injected liquids to react in hypergolic fashion and under the dynamics of molecular motion in the presence of a catalyst reform as CO2 and H2. After many micro-injections, the pressure will build up in this vessel. The gases formed are admitted into the Storage & Delivery system as needed in accordance with an algorithm stored in the FCPS. The Storage and delivery System will have a much larger volume than the reforming pressure

vessel and be of sufficient size to allow for delivery of sufficient H2 to support the Fuel Cell Stack power output

This process by having a second pressure vessel considerably larger than the first vessel connected via control valve takes advantage of a cooling phenomena with gasses. That is a known mass of gas mixture at pressure (P_1) and temperature (T_1) in vessel (1) as it expands into a second larger vessel (2) results in a lower pressure (P2) and temperature (T2) in that vessel. If the resulting temperature change should be insufficient, then a heat exchanger (HTX) installed in the delivery line (or in a heat exchange (HTX) jacket is an option to help achieve the need temperature.

This second vessel only has to hold enough mass of H2, at a sufficient pressure peculiar to the pressure regulator's operating range that allows the H2 system output to meet the operating points desired. The fuel cell stack H2 input will cover the maximum period when a vehicle is under maximum power draw. This is about 1 hour in an automotive environment. The Storage & Delivery Subsystem (Vessel 2) will start to be refilled from vessel 1 (the reforming/pressure vessel) when the sensor system indicates it has reach the design point for recharging. This would be in the vicinity of 20-25% of empty.

The output from this second vessel has a programmable pressure regulator valve coupled with an output valve (#4) thus controlling the pressure and flow into the

fuel cell stack. This flow can be either continuous or pulsed as a function of the pulse width command from the controller.

Figure 2 defines the operational flow of the Reformer Fuel Supply (sub) System. This figure shows as references the Fuel Cell power System Air Subsystem, Controller and the Reforming Pressure Vessel (#1). The function of this subsystem is to provide fuels that are hypergolic when combined/injected into the reforming & pressurizing vessel.

To accomplish this, two separate fueling tank systems will be required. The output for the individual liquids will be pumped to a pressure level that can be handled by the valves #1 and #2. It will also have a regulated return line to the tank to keep the pumps from over heating. Valves #1 & # 2 are the minimum number feasible for an operating system and said invention can have as many pairs of valves as needed in accord with the overall system design requirements.

The fueling pumps can be independently motored or driven by a shaft extension from the Air Subsystem drive motor. This later configuration would be the preferred one in an automotive environment since the Air subsystem motor is a FCPS need and the load imposed by the additional pumps for supplying fuel is relatively miniscule compared to driving the air compressor. Even with the reduction of power afforded to the air system needs by this invention, said air subsystem will still be the largest parasitic load on the FCPS.

Said valves (#1, &#2) will be high speed injector valves that allows the FCPS Controller to pulse inject the hypergolic reactants. The injecting valves will have a response speed such that the delivered fluid will be in the milliliter per millisecond region. This allows the FCPS controller to determine the rate of buildup of pressure and temperature internal to this vessel and use a pulse width modulation approach for controlling the "on time" of the delivery pulse, providing a very tight metering of fuel delivery. This same approach allows for delivery variation between each of the reactants as needed to achieve such things as a different mixture between the reactants in accord with the needs of the system relative to stoichiometric needs.

The HTP will be stored in a tank whose material construct must be nonreactive with HTP. Such material as PTFE is the currently recommended material as a tank or tank liner material. Similarly the Ethanol tank must not react with the liquid. There exist different compatible coatings for this type of tank and those skilled in the art are familiar with design of this type of tank. This tank has a fill port to accommodate a filling nozzle for HTP such as are currently used in industry. The tank output is pumped up to a pressure that will allow the injector to mist the reactants into the vessel#1. By mist injecting into the referenced Reforming Pressure Vessel, the number of ethanol molecules colliding with the HTP molecules in a given time frame is increased producing a faster reaction.

Figure 3 describes the Reforming Pressure Vessel (#1) functional operation and shows the interfacing parts of the Hypergolic Hydrogen Generating System along with the FCPS Controller. The Reforming Pressure Vessel (#1) is a high-pressure capable vessel. In it is a catalyst section whose material(s) are chosen to facilitate the formation of CO2 from the reactants injected via valves #1 & #2 in the Supply subsystem. Since the reaction is hypergolic, and its contents will increase in temperature and pressure, the vessel is provided with an over pressure relief valve or system, which will safely vent the pressure in case of system run away. The vessel has a sensor pack that provides pressure and temperature monitoring inside the vessel for use by the FCPS Controller. By knowing these values with the state of the other sections of the overall FCPS system the necessary commands are given to control the in letting of the reactants or to open valve #3 to output pressurized gas into the actual on board storage tank. It will do this until the storage pressure of vessel #2 is attained. Depending on the design sizing of various potential FCPS systems it may be necessary to provide a heat exchange system (HTX) as a stand alone entity between the reforming vessel and the storage vessel. It is also possible to provide such a function integral with the vessel itself. This is a matter of end systems use/needs and what can be achieved in the cooling brought about by expansion from the vessel #1 into the larger volume vessel #2.

Figure 4 shows the Storage & Delivery Subsystem with its related parts as well as reference interfacing segments of the balance Hypergolic Hydrogen Generating System and the FCPS stack & controller. The storage vessel portion of the system is considerably larger than the reformer vessel for the purposes of allowing the gases to cool as they expand into it. It also operates at a lower pressure to reduce the required range over which the pressure regulator must operate since the input maximum pressure requirement to the fuel cell stack needs to only balance the air pressure across the membrane. This pressure currently varies in most contemporary FCPS system designs from about 1.4 to 2.2 Pressure Ratio to ambient air. Even so the pressure in this tank is substantial, in the order of 2,000 psi, therefor the tank is provided with a pressure relief capability similar to the reformer subsystem. This tank is also provided with a sensor pack to provide pressure and temperature monitoring by the FCPS Controller. The pressure regulator is programmable by the FCPS Controller as a function of where in the Fuel Cell Stack output (voltage & Current) the pressure needs to be to effect best performance based upon demand by the load on the FCPS System.